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THE PROTON AFFINITIES OF SOME α,β-UNSATURATED ESTERS AND AMIDES

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ABSTRACT. — The proton affinity (PA) of the α,β-unsaturated esters methyl acrylate **1**, methyl methacrylate **2**, and methyl crotonate **3**, of the primary amides acrylamide **4**, methacrylamide **5**, and crotonamide **6**, and of the corresponding tertiary N,N-dimethyl amides **7, 8** and **9** has been determined from gas phase equilibrium measurements using FT-ICR spectroscopy. A comparison of the experimental results with MNDO calculations of the protomers **a, b** and **c** confirms protonation at the carbonyl-O atom in all cases. The effects of the ester amide group and of the methyl substituent at the C−C double bond on the PA are discussed.

The proton affinities, PA, and the heats of formation, ΔH_f, are fundamental data of organic compounds, in particular their dependence on the structure of the molecules permits a deep insight into the factors linking stability and reactivity to chemical bonding [1]. The PA's determined by gas phase basicity (GB) measurements reflect the properties of the molecules devoid any solvatation effects, and this is of special interest for studying polar substituent effects. Up to now the PA of some hundreds of compounds have been obtained and tabulated [2], but so far only a few α,β-unsaturated carbonyl compounds have been studied [3]. The conjugation of a C−O double bond and a C−C double bond should exert a marked effect on the PA of a carbonyl compound and on the ΔH_f of the protonated species. However, this effect is expected to depend strongly on the resonance energy gained by the conjugation which in turn depends on the presence of additional substituents at the carbonyl group and at the C−C double bond [3b]. To get more information about the interplay of these diverse effects on the PAs we have started an investigation of the GB's of some α,β-unsaturated esters and amides **1-9** (Fig. 1).

Y	$CH_2=CH_{CO\text{-}Y}$	$CH_2=C(CH_3)_{CO\text{-}Y}$	$CH_3\text{-}CH=CH_{CO\text{-}Y}$
OCH_3	1	2	3
NH_2	4	5	6
$N(CH_3)_2$	7	8	9

Figure 1.

It is known [2,4] that saturated esters and amides are protonated at the carbonyl group in the gas phase, although in the case of the amides the thermodynamic stabilities of the O- and N-protonated species may not be very different [5]. In solution it has been evidenced by NMR spectroscopy that both protomers **a** and **b** (Fig. 2) are formed depending on the structure of the individual amide [5c]. Besides the protomers **a** and **b** arising from a protonation at the carbonyl group and at the ether-O atom and the amide-N atom, respectively, the α-β-unsaturated esters and amides may also add the proton at the C−C double bond. This results in α-acyl carbenium ions **c**, and it has been shown by a systematic study of these destabilized carbenium ions that the protomer **c** is also a distinct species in the gas phase [6]. **c** is thermodynamically much less stable than **a** and **b**, but nevertheless a mutual interconversion between these protomers is observed at suitable internal energies. Thus, **c** may also formed by a reaction with a proton donor of sufficient acidity. The site of protonation of the α,β-unsaturated esters **1 - 3** and amides **4 - 9** can be verified by a comparison of the experimental $\Delta H_f(MH^+)$ derived from the PA of **1 - 9** with ΔH_f values calculated by MNDO for the pertinent protomers **a**, **b** and **c**.

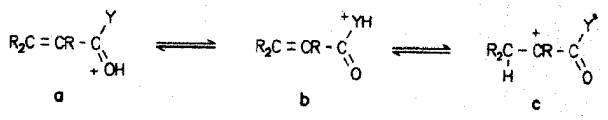

Figure 2.

Experimental

COMPOUNDS

The structures of all compounds used were verified by ^{1}H-NMR spectroscopy and 70eV EI-mass spectrometry, and the purity was controlled by appropriate chromatographic methods.

Methyl acrylate **1** and methyl methacrylate **2** were used as commercially available (purity < 98%). Methyl crotonate **3** was obtained by esterification of crotonic acid with methanol by standard procedures. Acrylamide **4** was prepared by stirring a solution of the corresponding acid chloride in 1,1-dichloro ethane with conc. aqueous NH_3 at − 10° C. Methacrylamide **5** and crotonamide **6** were synthesized by reaction of the corresponding acid chlorides with conc. aqueous NH_3 at − 10° C. The primary amides **4 - 6** were purified by recrystallisation. N,N-dimethyl acrylamide **7**, N,N-dimethyl methacrylamide **8**, and N,N-dimethyl crotonamide **9** were prepared by stirring a solution of the corresponding acid chloride in 1,1-dichloroethane and a mixture of excess $(CH_3)_2NH.HCl$ in 20% aqueous NaOH at − 10° C. The tertiary amides **7 - 9** obtained after separation of the organic phase and evaporation of the solvent were purified by distillation.

All compounds used as reference bases (see Tabl. I) were commercially available in pure form.

ICR SPECTROMETRY

The ICR experiments were performed with a Bruker Spectrospin CMS 47X FT-ICR instrument equipped with a 4.7 T superconducting magnet, a 24 bits/128 k-words Bruker Aspect 3000 computer and a cylindrical cell of 6 cm diameter. An internal ionization by 70 eV electrons and a filament current of 3.0-3.4 A was used. The ions were trapped by applying a potential of c. 1 V to the trapping plates. The total pressure within the ICR cell was $1 - 2 \times 10^{-6}$ mbar, read on the ion gauge in front of the high vacuum turbo pump and not corrected. The compound M to be studied and an appropriate reference base B were introduced into the ICR instrument controlling the partial pressures by the ion gauge and waiting for a constant reading. The ions were generated by an ionization pulse of 0.5 - 1.0 ms, and the ions MH^+ and BH^+ were formed by "self-CI". The ions MH^+ and BH^+, respectively, were isolated by a broad band ejection using JA/JINT = 12/60 - 80 as ejection parameters. Under these conditions the ejection is finished after 100 - 150 ms. Any ions besides MH^+ and BH^+ remaining in the cell after the broad band ejection were removed by "single shots" via a selective acceleration by appropriate single rf pulses. Following the ejection procedure the ion MH^+ and BH^+ were allowed to react with the neutral molecules for a variable reaction time until the ratio $[MH^+]/[BH^+]$ remained constant. The equilibrium was reached usually within 0.5 - 1.0 s. At the end of the reaction time all ions were excited by a broad band excitation with XA/XINT = 4/20 for detection. The value of the GB(M) was calculated from the measured free enthalpy of reaction, ΔG_r, according to equation (1), using the kown partial pressures of M and B, and the tabulated GB(B)[2]. A temperature T = 320 K was assumed in the ICR cell.

$$\Delta G_r = -RT\ln([MH^+][B]/[BH^+][M]) \quad (1)$$

Results and Discussion

The reference bases B used to determine the GB of **1 - 9** (= M) by the well established techniques of gas phase equilibrium measurements [7], the values of GB(B)[2] based on $GB(NH_3)$ = 823 kJ.mol^{-1}, the experimental values of ΔG_r, and the GB(M) and PA(M) derived therefrom are given in Table I. The PA(M) have been calculated from the corresponding GB(M) by correcting for the translational entropy of the free proton (− 32 kJmol^{-1} at 293 K[8]). This procedure is correct as long as no protonation at the C − C double bond of **1 - 9** occurs. This latter reaction is not observed as shown in the following discussion. By a careful choice of the reference base B, the maximum value of ΔG_r does not exceed ± 6 kJ.mol^{-1} and the reproducibility of ΔG_r is < 0.5 kJ.mol^{-1} in most cases. However, the experimental error of ΔG_r (and correspondingly of GB(M) and PA(M), respectively) is estimated to be ± 1 kJ.mol^{-1} because of an uncertainty in measuring the sample pressure in the ICR cell.

The effects of the substituent Y (= − OCH_3, − NH_2, − $N(CH_3)_2$) at the carbonyl group and the methyl substituents at the C − C double bond are seen from a comparison of the PA of **1 - 9** and some α,β-unsaturated aldehydes, ketones and carboxylic acids [3b] with those of their saturated analogues [2] (Tabl. II).

The *effect of Y at the carbonyl group* on the PA is quite uniform for the three types of α,β-unsaturated carbonyl compounds. For the unsaturated compounds the PA increases in the order Y = H, CH_3, OH, OCH_3, NH_2, $N(CH_3)_2$ *relative* to the aldehydes (Y = H) by 31 ± 4, 5 ± 7, 21 ± 5, 56 ± 7, 89 ± 1 kJ.mol^{-1}, respectively. The large increase of the PA due to the H_2N- and $(CH_3)_2N$-substituent reflects the large GB of the amide group known from saturated amides [2]. The enhancement by a CH_3O group is much less because of the opposing inductive and resonance effects also observed in the case of the carboxylic acids (Y = OH) [3b]. In fact the incidence of HO- and CH_3O-substitution at the carbonyl group on the PA of the α,β-unsaturated compounds is distinctly less than for the saturated analogues (ester: unsaturated ΔPA = + 21 ± 5, saturated + 38 ± 6; acid: unsaturated ΔPA = 5 ± 7, saturated ΔPA = + 11 ± 3 kJ.mol^{-1}).

A comparison of the PA of acrolein, 3-buten-2-one, acrylic acid, methyl acrylate **1**, acrylamide **4** and N,N-dimethyl acrylamide **7** to the PA of their saturated analogues (Tabl. II) demonstrates clearly that the *effect of the conjugated C − C double bond* is not uniform and depends strongly on the substituent Y at the carbonyl group. Acrolein and acrylic acid are more basic than propionaldehyd and propionic acid, respectively, as expected considering a stabilization of the protonated α,β-unsaturated carbonyl compounds by a delocalization of the positive charge within the conjugated π-system (Fig. 3):

However, this effect is already small in the case of 3-buten-2-one and butan-2-one, and methyl acrylate **1** is definitely

Table I. − Gas phase basicities GB(B) of the reference bases [2], ΔG_r of the proton transfer reaction, gas phase basicities GB(M) and proton affinities PA(M) of the α,β-unsaturated esters **1 - 3** and amides **4 - 9** (in kJ.mol^{-1}).

Compound M	Reference base B	GB(B)	ΔG_r	GB(M)	PA(M)
1, $CH_2=CH-COOCH_3$	tetrahydrofurane	801	+0.3	801	833
	cyclopentanone	801	+0.3	801	833
2, $CH_2=C(CH_3)COOCH_3$	3-methyl-2-butanone	809	+1.9	811	843
	methyl acetate	807	+4.0	811	843
3, $CH_3-CH=CH-COOCH_3$	dimethoxyethane	819	+0.6	820	851
4, $CH_2=CH-CONH_2$	2-phenylpropene	833	+3.9	837	869
	4-methylacetophenone	840	−3.4	837	869
5, $CH_2=C(CH_3)-CONH_2$	aniline	847	−1.3	846	878
	4-methylacetophenone	840	+5.9	846	878
6, $CH_3-CH=CH-CONH_2$	benzophenone	850	+2.7	853	884
	N,N-dimethylformamide	852	+0.4	852	883
7, $CH_2=CH-CON(CH_3)_2$	benzylamine	874	−5.8	868	900
8, $CH_2=C(CH_3)-CON(CH_3)_2$	benzylamine	874	+1.4	875	907
9, $CH_3-CH=CH-CON(CH_3)_2$	*t*.butylamine	891	+0.2	891	924
	pyridine	891	+0.8	892	925

Table II. – Proton affinities (in kJ.mol^{-1}) of α,β-unsaturated carbonyl compounds and of their saturated analogues.

Compound	PA	δ[a]	Compound	PA	δ[a]
$CH_2=CH-CHO$	811[2]	–	CH_3-CH_2-CHO	793[2]	–
$CH_2=CH-CO-CH_3$	838[2]	–	$CH_3-CH_2-CO-CH_3$	836[2]	–
$CH_2=CH-CO-OH$	820[3b]	–	$CH_3-CH_2-CO-OH$	802[2]	–
1, $CH_2=CH-CO-OCH_3$	833	–	$CH_3-CH_2-CO-OCH_3$	838[2]	–
4, $CH_2=CH-CO-NH_2$	869	–	$(CH_3-CO-NH_2$	863[2])	–
7, $CH_2=CH-CO-N(CH_3)_2$	900	–	$(CH_3-CO-N(CH_3)_2$	907[2])	–
$CH_2=C(CH_3)-CHO$	817[2]	+ 6	$CH_3-CH(CH_3)-CHO$	806[2]	+13
$CH_2=C(CH_3)-CO-CH_3$	851[2]	+13	$CH_3-CH(CH_3)-CO-CH_3$	841[2]	+ 5
$CH_2=C(CH_3)-CO-OH$	825[3b]	+ 5	$CH_3-CH(CH_3)-CO-OH$	820	+18
2, $CH_2=C(CH_3)-CO-OCH_3$	843	+10	$CH_3-CH(CH_3)-CO-OCH_3$	843[2]	+ 5
5, $CH_2=C(CH_3)-CO-NH_2$	878	+ 9	–	–	–
8, $CH_2=C(CH_3)-CO-N(CH_3)_2$	907	+ 7	–	–	–
$CH_3-CH=CH-CO-CH_3$	867[2]	+29	–	–	–
$CH_3-CH=CH-CHO$	835[2]	+24	$CH_3-CH_2-CH_2-CHO$	801[2]	+ 8
$CH_3-CH=CH-CO-OH$	833[3b]	+13	$CH_3-CH_2-CH_2-CO-OH$	812	+10
3, $CH_3-CH=CH-CO-OCH_3$	851	+18	$CH_3-CH_2-CH_2-CO-OCH_3$	837[2]	– 1
6, $CH_3-CH=CH-CO-NH_2$	884	+15	–	–	–
9, $CH_3-CH=CH-CO-N(CH_3)_2$	924	+24	–	–	–

[a] Methyl group effect (kJ.mol^{-1}), variation of PA by the methyl substituent.

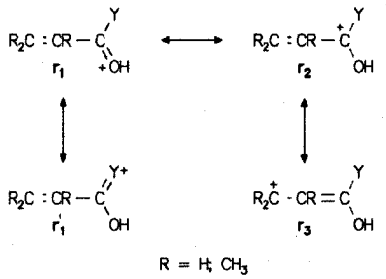

Figure 3.

less basic than its saturated analogue methyl propionate. The PA's of propionamide and N,N-dimethyl propionamide are not known, but from the PA(acetamide) = 863 kJ.mol^{-1} and PA (N,N-dimethylacetamide) = 907 kJ.mol^{-1} [2] one can estimate that the PA's of the acrylamides **4** and **7** are probably also less than those of their saturated analogues. Thus, the enhancement of the PA of the carbonyl compound by the α,β-unsaturation levels off with increasing basicity of the moiety containing the carbonyl group and eventually turns to a diminution of the PA.

One explanation for the different behaviour of the α,β-unsaturated carbonyl compounds on protonation would be that only the α,β-unsaturated aldehydes, ketones and carboxylic acids are carbonyl-protonated while in the case of the more basic esters and amides the protonation occurs at the ether-O atom and the amide-N atom, respectively, generating the protomer **b**. In this case the positive charge is localized at the protonated atom and no stabilization by resonance is possible. This can be explored by a comparison of the experimental heats of formation, $\Delta H_f(MH^+)$, with the ΔH_f's calculated by MNDO for the protomers **a**, **b** and **c** (Fig. 2). The heat of formation, ΔH_f, of protonated α,β-unsaturated esters and amides is derived from the experimental PA by equation (2):

$$\Delta H_f(MH^+) = \Delta H_f(M) - PA(M) + \Delta H_f(H^+) \qquad (2)$$

$\Delta H_f(H^+)$ = 1528 kJ.mol^{-1} is a well know quantity [9], but unfortunately experimental $\Delta H_f(M)$'s are only tabulated [10] for **1** and **3**, and there are no increments available to estimate $\Delta H_f(M)$ with the aid of Benson's compilation [11]. As a surrogate the $\Delta H_f(M)$ for **1** - **9** have been calculated by MNDO [12] which is known, however, to suffer from systematic errors for some organic molecules and ions [13]. Indeed, the comparison of the calculated (Tabl. III) and the experimental values for **1** (– 333 kJ.mol^{-1}) and **3**(– 343 kJ.mol^{-1}) reveal that MNDO calculates the $\Delta H_f(M)$ to high by 50 and 19 kJ.mol^{-1}, respectively. A similar deviation of the MNDO values of ΔH_f

Table III. – Heat of formation, ΔH_f, (kJ.mol^{-1}) of MH^+ calculated from the PA and by MNDO.

Compound	ΔH_f (M)[a]	ΔH_f (MH^+)	ΔH_f (a)[a]	ΔH_f (b)[a]	ΔH_f (c)[a]
1, $CH_2=CH-CO-OCH_3$	–283	412	402	518	608
2, $CH_2=C(CH_3)-CO-OCH_3$	–314	370	380	487	542
3, $CH_3-CH=CH-CO-OCH_3$	–324	353	374	471	534
4, $CH_2=CH-CO-NH_2$	–103	556	560	628	790
5, $CH_2=C(CH_3)-CO-NH_2$	–134	509	527	602	726
6, $CH_3-CH=CH-CO-NH_2$	–144	499	514	583	766
7, $CH_2=CH-CO-N(CH_3)_2$	– 77	550	572	655	797
8, $CH_2=C(CH_3)-CO-N(CH_3)_2$	–106	514	541	628	738
9, $CH_3-CH=CH-CO-N(CH_3)_2$	–119	485	526	610	776

[a] Calculated by MNDO.

has to be expected not only for the other α,β-unsaturated neutral carbonyl compounds but also for the corresponding protonated species **a** - **c**. Hence, the systematic errors of a MNDO calculation are offset to some extent in a comparison of $\Delta H_f(MH^+)$ from equation (2) and of ΔH_f of **a**, **b** and **c**.

In all cases the MNDO calculations show that the protomer **a** is the most stable one [14]. The species **b** protonated at the methoxy-O atom of the ester group and the amino-N atom of the primary and tertiary amide group is thermodynamically less stable by *c.* 105 kJ.mol^{-1}, *c.* 70 kJ.mol^{-1} and *c.* 85 kJ.mol^{-1}, respectively. Likewise, the ΔH_f of the C-protonated species **c**, corresponding to destabilized α-acyl carbenium ion [6], is raised in most cases by more than 200 kJ.mol^{-1}. The values of $\Delta H_f(MH^+)$ derived from the experimental PA by equation (2) agree reasonably well with ΔH_f(**a**) in all cases confirming a protonation of the α,β-unsaturated esters **1** - **9** at the carbonyl-O atom. It should be reminded that this is only true for a protonation by weak acids in an equilibrium experiment, and that in the case of a CI experiment with CH_5^+ a protonation of all basic centers of **1** - **9** is possible due to the high gas phase acidity of the reagent ion. However, the present results clearly demonstrate that the different effects of α,β-unsaturation on the PA of carbonyl compounds with different substituents at the carbonyl group are not due to different sites of protonation.

Qualitatively, the effect of an α,β-unsaturation can be rationalized by a consideration of the different resonance formulae of the protonated α,β-unsaturated carbonyl compounds (Fig. 3). In the series $CH_2=CH-CO-Y$ and compared to the saturated analogues, the resonance structure r_3 explaining the increase of the PA of acrolein (Y = H) is obviously less important for the protonated 3-buten-2-one (Y = CH_3) and unimportant for **1** (Y = OCH_3), **4** (Y = NH_2), and **7** (Y = $N(CH_3)_2$). The positive charge is stabilized in protonated 3-buten-2-one mostly according to r_2 by the inductive effect (+ I) of the methyl group, and in the latter compounds by a charge delocalization ($r_1 - r_1'$) within the protonated ester group and amide group, respectively. Then, the decrease of the PA of **1**, (and probably of **4** and **7**) must be due to − I effect of the vinyl group.

The saturated carbonyl compounds exhibit a distinct *"methyl group" effect* (δ in Tabl. II), a methyl substituent at the α-position to the carbonyl group increasing the PA by 5-13 kJ.mol^{-1}. This effect is much smaller for a β-methyl substituent as expected, and in fact the PA's of methyl propionate and methyl butyrate are nearly identical. It has been noted before [3b], that the unsaturated carbonyl compounds behave differently. While the increase of the PA due to an α-methyl group is of the same magnitude as in the case of the saturated carbonyl compounds, a β-methyl substituent enhances the PA of α,β-unsaturated aldehydes and ketones by 24 ± 8 kJ.mol^{-1} [3b]. This is of course easily explained by a + I effect of that methyl group on the resonance structure r_3. However, the enhancing effect of a β-methyl substitution on the PA of α,β-unsaturated carboxylic acids is only 5-13 kJ.mol^{-1} [3b] indicating again that r_3 is less important if the positive charge is distributed by resonances within the carbonyl functionality. An analogous or even more pronounced diminution of the β-methyl effect is expected for α,β-unsaturated ester **3** and amides **6** and **9**. However, the experimentally observed effects fall into the region between the effects observed for ketones and acids. This shows in particular that the PA of an α,β-unsaturated carbonyl compound arises from a delicate balance between the different resonance and inductive effects which are certainly not additive. Hence it appears rather difficult to predict quantitatively the PA of an individual α,β-unsaturated carbonyl compound by a simple model although it appears possible to "rationalize" the variations of the PA by a discussion of inductive, poplarizability, and resonance effects.

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[14] Only the ΔH_f of the most stable conformer is given. As has been pointed out by a referee *cis/trans*-isomers exist for each of the protomers as well as *syn/anti*-conformers with respect to the orientation of the newly formed OH group. However, in view of the limited reliability of MNDO a discussion of these conformational effects on the ΔH_f's would be an overinterpretation of the computational results.